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C-METHYL PHENOLICS FROM *QUALEA* SPECIES*

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Key Word Index—*Qualea labouriauana*; *Q. paraensis*; Vochysiaceae; *C*-methylflavanones; *C*-methylbenzophenone.

Abstract—The trunk wood of *Qualea labouriauana* contains, besides (2*R*)-5,7,4′-trihydroxy-3′-methoxy-6,8-dimethylflavanone, (2*R*)-5,7,4′-trihydroxy-8-methylflavanone, the biosynthetically interesting 2,2′-dihydroxy-4,6,4′,6′-tetramethoxy-3,3′-dimethylbenzophenone. From the trunk wood extract of *Q. paraensis* the first named flavanone crystallized out directly.

INTRODUCTION

Previous publications report the presence of ellagic acid and five derivatives and of 7,3′,4′-trihydroxyflavone and three derivatives respectively in the wood of *Erisma calcaratum* (Link) Warm., *Salvertia convallariodora* St. Hil., *Vochysia acuminata* Bongard, *V. tyrsoidea* Pohl. [1] and in the leaves of *S. convallariodora*, *V. cinnamomea* Pohl., *V. tucanorum* Mart. [2]. The present communication reports the presence of the *C*-methylated flavanones **1a**, **2a**, **3a** and benzophenone **4a** in the wood of *Qualea labouriauana* Paula [3]. (2*R*)-5,7,4′-Trihydroxy-3′-methoxy-6,8-dimethylflavanone (**1a**) was also isolated from *Q. paraensis* Ducke [4], a further South American species of the Vochysiaceae.

RESULTS

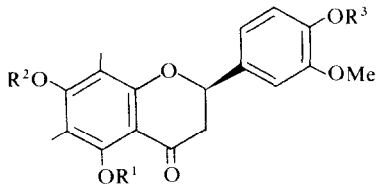
Compounds **1a** and **2a** are (2*R*)-flavanones as shown by ORD curves [5] and the typical NMR signals for the protons at C-2 and C-3 [6]. Due to the slight solubility of **1a** in the usual deuterated solvents the NMR spectral analysis referred to dimethyl (**1b**), diethyl (**1d**) and dibenzyl (**1e**) ethers, as well as to di-(**1f**) and tri-(**1g**) acetates. Interpretation of all signals led to the formula $C_{15}H_6O_2(OH)_3OMe.Me_2$ for the natural compound. The presence of hydroxyls at C-5 and C-7 was ascertained by UV shifts, respectively with $AlCl_3$ and NaOAc. The action of $AlCl_3$ is not instantaneous, a fact which, together with the inertness towards etherification and even acetylation, indicates the steric hindrance of the 5-hydroxyl by the methyl group at C-6. The other methyl is located at C-8 since the three aromatic protons, forming an ABX-system, must all be located on ring B. The 270 MHz spectrum shows the X-part, at the low field end of the signal (τ 2.76 for **1b**), as a doublet (J = 3 Hz) which apears in the triacetate (**1g**) at slightly higher field ($\Delta\tau$ + 0.08 ppm). The AB-part (τ *ca* 3.15 for **1b**) is resolved in **1g** into a doublet ($\Delta\tau$ −0.20, J = 8 Hz) and a double doublet ($\Delta\tau$ −0.06, J = 8, 3 Hz). These facts indicate that all protons are *ortho* or *para* related with only one oxy-function and that it is the proton which is coupled only to an *ortho*-proton which is vicinal to the OH group in **1a**. The usual 4′-hydroxy-3′-methoxy B ring pattern thus prevails in the compound.

The ^{1}H NMR spectra of **2a**, $C_{15}H_8O_2(OH)_3Me$, and of poriol (**2b**) [7, 8], though not identical, are very similar. The mps, however, are quite distinct: **2a** 195–200°, **2b** 265–270° [7]. Since both products show identical ORD curves (for **2b** see [9]), they can differ only by the location of the A ring methyl.

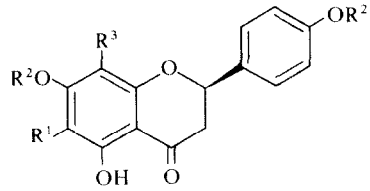
Compound **3a** is a (2*S*, 3*S*)-dihydroflavonol, as shown by an ORD curve [5] and the typical NMR signals for the protons at C-2 and C-3 [6]. The 4′-hydroxy pattern for ring B is evidenced by the AA′BB′ signals shifted to substantially lower field upon acetylation to **3b**. The reaction gives also evidence for the hydroxyl at C-3 [$\Delta\tau$ −0.72 ppm (H-2), −1.33 ppm (H-3)]. Indeed, the UV $AlCl_3$ shift is reversed upon addition of HCl, a fact which is inconsistent with the existence of a hydroxyl at C-5. The IR carbonyl maximum at 1675 cm^{-1} is also compatible with a 3-hydroxy-5-methoxyflavanone [10]. 3,5-Dihydroxyflavanones show that absorption at 1620–1640 cm^{-1} [10, 11]. The remaining hydroxyl must be located at C-7 (UV NaOAc shift). This leaves only C-6 or C-8 for the methyl, the former location being preferred tentatively on account of the neatness of the aromatic singlet (τ 3.83). The methoxyl protons would be expected to cause broadening of the H-6 signal [12].

The molecular formula of **4a**, $C_{19}H_{22}O_7$, determined by HRMS, was expanded to $C_{12}H_2(OH)_2(OMe)_4Me_2CO$ after inspection of the ^{1}H NMR spectrum which shows only five singlets at τ 2.1 (OH), 3.9 (ArH), 6.0 (ArOMe), 6.2 (ArOMe) and 7.98 (ArMe). The compound must thus possess a symmetrical benzophenone structure, a fact which is consistent with its UV spectrum [13]. The aromatic proton singlet at

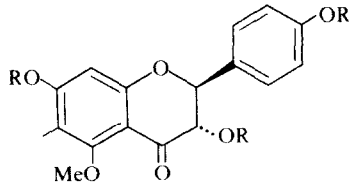
* Part II in the series "The Chemistry of Brazilian Vochysiaceae". For Part I see ref. [1]. Based on part of the M.S. thesis submitted by L.F.B.G. to Universidade Federal de Minas Gerais (1979).



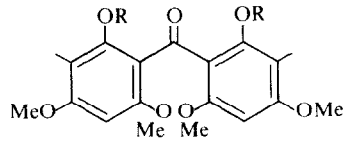
1a $R^1 = R^2 = R^3 = H$
1b $R^1 = H$, $R^2 = R^3 = Me$
1c $R^1 = R^3 = H$, $R^2 = Et$
1d $R^1 = H$, $R^2 = R^3 = Et$
1e $R^1 = H$, $R^2 = R^3 = CH_2Ph$
1f $R^1 = H$, $R^2 = R^3 = Ac$
1g $R^1 = R^2 = R^3 = Ac$



2a $R^1 = R^2 = H$, $R^3 = Me$
2b $R^1 = Me$, $R^2 = R^2 = H$
2c $R^1 = H$, $R^2 = R^3 = Me$
2d $R^1 = R^{2'} = Me$, $R^3 = H$



3a R = H
3b R = Ac



4a R = H
4b R = Ac

relatively high field points to the existence of phloroglucinol patterns. The hydroxyls are both chelated (UV/$AlCl_3$ shift) and highly hindered, acetylation of the compound leading only to a diacetate (**4b**) and in low yield. The sole structure **4a** which is compatible with these data is corroborated by the ^1H NMR spectrum of this acetate which shows singlets at τ 3.58 and 3.65 (2 ArH), 6.2 (4 ArOMe), 7.72 and 7.82 (2 ArOAc), 8.16 and 8.17 (2 ArMe). Chelation having ceased, repulsion of the acetoxyl groups causes the asymmetry of the rings with respect to the carbonyl which is now observed.

DISCUSSION

The unifying feature of the compounds from these *Qualea* species is the substitution of the acetate derived phloroglucinol units by *C*-methyls. Specially interesting is the benzophenone in which two such units are joined by a carbonyl group. This group, however, may also have originated from a *C*-methyl, formation of the compound involving oxidative coupling of dimethylated and monomethylated phloroglucinol analogues.

EXPERIMENTAL

Isolation of the constituents from Qualea labouriauana. Plant material was collected in the vicinity of Parintins, Amazonas State, and identified by Dr. José Elias de Paula (voucher IAN, Belém, 99910). Ground trunk wood was extracted successively with C_6H_6 and EtOH. The C_6H_6 extract (10 g) was separated by Si gel (500 g) column chromatography into 3 useful fractions eluted with C_6H_6–$CHCl_3$–MeOH of respective proportions 7:3:0, 1:1:0 and 0:97:3. The 1st fraction gave, by re-chromatography and crystallization from EtOH, **4a** (10 mg). The 2nd fraction gave, by washing with MeOH and recrystallization from MeOH, sitosterol (900 mg). The 3rd fraction gave, by re-chromatography (Sephadex LH-20, MeOH), **1a** (250 mg). The EtOH extract (160 g) was adsorbed on Si gel (500 g). Washing with $CHCl_3$–MeOH 7:3 gave a product (100 g) which was separated by Si gel (800 g) column chromatography into 2 useful fractions eluted with $CHCl_3$–MeOH of respective proportions 99:1 and 9:1. The 1st fraction gave, by washing with Et_2O, **1a** (150 mg). The 2nd fraction gave, by washing with Et_2O and purification by TLC, **3a** (30 mg). All residual material stemming from the EtOH extract was united and extracted with AcOEt. The extract (90 g) was separated by Si gel (600 g) column chromatography into one useful fraction eluted with $CHCl_3$–MeOH 98:2. This gave, by repeated TLC, **2a** (50 mg).

Isolation of the constituents from Qualea paraensis. Plant material was collected and identified by Dr. José Elias de Paula. Ground trunk wood (7.3 kg) was extracted with C_6H_6. The solution deposited, upon concn and cooling, crystals of **1a** (2 g) which were separated by filtration.

(2*R*)-5,7,2′-*Trihydroxy*-4′-*methoxy*-6,8-*dimethylflavanone* (**1a**). Mp 218–220° (M Found: 330.1091; $C_{18}H_{18}O_6$ Requires: 330.1103). ν_{max}^{KBr} cm^{-1}: 3390, 3200, 1635, 1600, 1510. λ_{max}^{EtOH} nm: 330, 350 (ε 9750, 2000); $\lambda_{max}^{EtOH+NaOAc}$ nm: 234 inf., 258, 300 inf., 345 (ε 4600, 1650, 3800, 12400); $\lambda_{max}^{EtOH+NaOH}$ nm: 228, 243, 343 (ε 9100, 6950, 15350); $\lambda_{max}^{EtOH+AlCl_3}$ nm (after 15 min): 303, 365 (ε 16500, 4950). MS (*m/e*): 330 (42%) M^+, 312 (100), 207 (5), 181 (63), 180 (8), 152 (27), 150 (22), 149 (12), 135 (23), 124 (11). *Dimethyl ether* (**1b**), mp 138–140 (EtOH). ν_{max}^{KBr} 3420, 1635, 1590, 1500. λ_{max}^{EtOH} nm: 288, 365 (ε 12900, 2700); $\lambda_{max}^{EtOH+NaOH}$ nm: 292 (ε 9850); $\lambda_{max}^{EtOH+AlCl_3}$ nm: 296 (ε 9400). ^1H NMR ($CDCl_3$, 270 MHz): τ −2.06 (*s*, OH-5), 2.76 (*d*, $J \sim 3$ Hz, H-2′), ~3.1 (*m*, H-5′, H-6′), 4.41 (*dd*, $J = 12$, 3 Hz, H-2), 7.04 (*dd*, $J = 16$, 3 Hz, H-3 eq), 7.15 (*dd*, $J = 16$, 12 Hz, H-3 ax), 7.89, 7.90 (2 *s*, 2 OAc). MS (*m/e*): 358 (100%) M^+, 195 (8), 194 (32), 166 (39), 164 (92), 149 (29). *Ethyl ethers* (**1a**, Et_2SO_4, K_2CO_3, Me_2CO, reflux, 56 hr; the product was separated by dry Si gel column chromatography into **1d** (30 parts), eluted with C_6H_{14}–C_6H_6 3:7 and **1c** (1 part) eluted with $CHCl_3$–MeOH, 1:1). **1c**, mp 200 (C_6H_{14}–Et_2O, 1:1). ν_{max}^{KBr} cm^{-1}: 3240, 1630, 1600. λ_{max}^{EtOH} nm: 292, 367 (ε 9550, 5500);

$\lambda_{max}^{EtOH+NaOAc}$ nm: 292, 370 (ε 9300, 5200); $\lambda_{max}^{EtOH+NaOH}$ nm: 296 (ε 4050); $\lambda_{max}^{EtOH+AlCl_3}$ nm: 290, 375 (ε 9550, 5800). ^{1}H NMR [$(CD_3)_2CO$, 60 MHz]: τ −2.13 (*s*, OH-5), 1.60 (*s*, OH-4′), 2.80–3.20 (*m*, H-2′, 5′, 6′), 4.20 (*dd*, *J* = 11, 5 Hz, H-2), 6.05 (*q*, *J* = 7 Hz, OCH_2-7), 6.20 (*s*, OMe-3′), 6.87–7.10 (*m*, *J* = 11, 5 Hz, H-3), 7.90 (*s*, 2 Me), 8.59 (*t*, *J* = 7 Hz, Me). MS (*m/e*): 358 (88%) M^+, 340 (100), 325 (56), 312 (25), 297 (32), 209 (49), 181 (41), 180 (11), 152 (16), 150 (21), 135 (23), 29 (30). **1d**, mp 110° (MeOH). ν_{max}^{KBr} cm^{-1}: 3400, 1630, 1620, 1500. λ_{max}^{EtOH} nm: 290, 365 (ε 13300, 9250); $\lambda_{max}^{EtOH+NaOH}$ nm: 295 (ε 13700). ^{1}H NMR (CCl_4, 60 MHz): τ −1.93 (*s*, OH-5), 2.90–3.32 (m, H-2′, 5′, 6′), 4.39 (*dd*, *J* = 11, 5 Hz, H-2), 6.00, 6.24 (2 *q*, *J* = 7 Hz, 2 OCH_2), 6.27 (*s*, OMe-3′), 6.90–7.34 (*m*, 2 H-3), 7.95 (*s*, 2 Me), 8.60, 8.75 (2 *t*, *J* = 7 Hz, 2 Me). MS (*m/e*): 386 (100%) M^+; 209 (9), 208 (33), 181 (10), 180 (15), 178 (94), 177 (8), 152 (22), 150 (26), 149 (14), 135 (16), 29 (16). *Dibenzyl ether* (**1e**), mp 130° (cyclohexane). ν_{max}^{KBr} (cm^{-1}): 3400, 1630, 1580, 1500. λ_{max}^{EtOH} nm: 292, 365 (ε 10950, 2300); $\lambda_{max}^{EtOH+NaOH}$ nm: 250 inf., 296, 392 (ε 13260, 13260, 5860); $\lambda_{max}^{EtOH+AlCl_3}$ nm: 293, 367 (ε 9950, 2300). ^{1}H NMR ($CDCl_3$, 60 MHz) τ: −2.00 (*s*, OH-5), 2.59, 2.65 (2 *s*, 2 Ph), 2.76–3.13 (*m*, H-2′, 5′, 6′), 4.24 (*dd*, *J* = 10, 7 Hz, H-2), 4.93, 5.15 (2 *s*, 2 OCH_2), 6.20 (*s*, OMe), 6.90–7.28 (*m*, *J* = 10, 7 Hz, H-3), 7.90 (*s*, 2 Me). MS (*m/e*): 510 (92%) M^+, 492 (10), 420 (16), 402 (36), 312 (20), 271 (10), 240 (10), 181 (30), 180 (19), 152 (9), 150 (19), 149 (20), 92 (53), 91 (100). *Diacetate* (**1f**) (**1a**, Ac_2O, C_5H_5N, room temp.), mp 98–100°. ν_{max}^{KBr} cm^{-1}: 3440, 1760, 1630, 1600, 1500. λ_{max}^{EtOH} (nm): 282, 367 (ε 12600, 5600); $\lambda_{max}^{EtOH+AlCl_3}$ nm (after 15 min): 288, 309, 380 (ε 10550, 8300, 4350). ^{1}H NMR ($CDCl_3$, 60 MHz): τ −2.03 (*s*, OH-5); 2.84–3.00 (*m*, H-3′, 5′, 6′), 4.55 (*dd*, *J* = 11, 5 Hz, H-2), 6.17 (*s*, OMe-4′), 6.95–7.25 (*m*, *J* = 11, 5 Hz, H-3), 7.64 (*s*, OAc-7), 7.74 (*s*, OAc-2′), 8.00, 8.05 (2*s*, 2 Me). MS (*m/e*): 414 (50%) M^+, 372 (18), 354 (100), 312 (81), 181 (35), 180 (15), 152 (17), 150 (17), 135 (12), 43 (39). *Triacetate* (**1g**) (**1a**, Ac_2O, C_5H_5N, steam bath), mp 176–178° (cyclohexane). ν_{max}^{KBr} cm^{-1}: 1760, 1685, 1600, 1500. λ_{max}^{EtOH} nm: 263, 336 (ε 10700, 5250). ^{1}H NMR ($CDCl_3$, 270 MHz): τ 2.85 (*d*, *J* = 3 Hz, H-2′), 2.95 (*d*, *J* = 8 Hz, H-5′), 3.09 (*dd*, *J* = 8, 3 Hz, H-6′), 4.65 (*dd*, *J* = 13, 3 Hz, H-2), 6.17 (*s*, OMe-4′), 7.02 (*dd*, *J* = 15, 13 Hz, H-3 ax), 7.27 (*dd*, *J* = 15, 3 Hz, H-3 eq), 7.59, 7.64, 7.74 (3 *s*, 3 OAc), 7.97, 8.05 (2 *s*, 2 Me).

(2*R*)-5,7,4′-*Trihydroxy*-8-*methylflavanone* (**2a**), mp 195–200° (M Found: 286.0847; $C_{16}H_{14}O_5$. Requires: 286.0841), ν_{max}^{KBr} cm^{-1}: 3500, 3400–3050, 1635, 1610. λ_{max}^{EtOH} nm: 300, 340 (ε 9600, 2600); $\lambda_{max}^{EtOH+NaOAc}$ nm: 232, 257 inf., 287 inf., 337 (ε 9300, 2850, 2400, 12700); $\lambda_{max}^{EtOH+NaOH}$ nm: 230, 275, 335 (ε 11000, 11850, 14300); $\lambda_{max}^{EtOH+AlCl_3}$ nm: 315, 355 (ε 9900, 1000). ^{1}H NMR ($(CD_3)_2CO$, 60 MHz) comparison of **2a**/**2b** [7]: τ −2.38/−0.21 (*s*, OH-5), 2.66/2.72, 3.18/3.21 (AA′BB′-system, *J* = *ca* 9 Hz, H-2′, H-6′ and H-3′, H-5′), 4.01/4.04 (*s*, H-6/H-8), 4.59/4.68 (*dd*, *J* = 12, 4 Hz, H-2), 6.35–7.45 (*m*, 2 H-3), 8.06/8.04 (*s*, Me-8/Me-6). MS (*m/e*): 286 (100%) M^+, 285 (32), 193 (14), 167 (67), 166 (40), 138 (47), 120 (25), 119 (8), 110 (10). *Dimethyl ether* (**2c**), mp 103–106° (**2d**, mp [7, 8] 147–148°) ν_{max}^{KBr} cm^{-1}: 3425, 1640, 1615. λ_{max}^{EtOH} nm: 298, 344 (ε 8800, 1900); $\lambda_{max}^{EtOH+NaOAc}$ nm: 229, 295, 350 (ε 18800, 8800, 2200); $\lambda_{max}^{EtOH+NaOH}$ nm: 230, 250 inf., 295, 370 (ε 8500, 3800, 4700, 3800); $\lambda_{max}^{EtOH+AlCl_3}$ nm: 310, 365 (ε 9100, 3140). ^{1}H NMR ($CDCl_3$, 60 MHz): τ −2.03 (*s*, OH-5), 2.60, 3.05 (AA′BB′-system, *J* = *ca* 9 Hz, 3.90 (*s*, H-6), 6.14 (*s*, 2 OMe), 8.00 (*s*, Me-8). MS (*m/e*): 314 (92%) M^+, 313 (27), 207 (14), 181 (16), 180 (100), 152 (70), 134 (93), 124 (10), 119 (23).

(2S, 3S)-3,7,4′-*Trihydroxy*-5-*methoxy*-6-*methylflavanone* (**3a**), mp 234–236°. (M Found: 316.0958; $C_{17}H_{16}O_6$. Requires: 316.0947.) ν_{max}^{KBr} cm^{-1}: 3360, 3280, 1675, 1600. λ_{max}^{MeOH} nm: 290, 340 (ε 9800, 6300); $\lambda_{max}^{MeOH+NaOAc}$ nm: 335 (ε 12650). $\lambda_{max}^{MeOH+NaOH}$ nm: 335 (ε 14200); $\lambda_{max}^{MeOH+AlCl_3}$ nm: 320 (ε 13250). ^{1}H NMR ($(CD_3)_2SO$, 60 MHz: τ 2.68, 3.24 (AA′BB′-system, *J* = *ca* 9 Hz, H-2′, H-6′ and H-3′, H-5′), 3.83 (*s*, H-8), 5.07 (*d*, *J* = 10 Hz, H-2), 5.78 (*d*, *J* = 10 Hz, H-3), 6.27 (*s*, OMe-5), 8.18 (*s*, Me-6). MS (*m/e*): 316 (5%) M^+; 287 (17), 181 (93), 180 (100), 165 (8), 152 (20), 151 (15), 137 (25), 136 (23), 122 (99), 107 (28). *Triacetate* (**3b**), mp 78–80° (C_6H_{14}). ν_{max}^{KBr} cm^{-1}: 1760, 1700, 1600, 1575, 1500. λ_{max}^{EtOH} nm: 280, 337 (ε 16600, 9300). ^{1}H NMR ($CDCl_3$, 60 MHz): τ 2.50, 2.90 (AA′BB′-system, *J* = *ca* 9 Hz, H-2′, H-6′ and H-3′, H-5′), 3.70 (*s*, H-8), 4.35 (*d*, *J* = 12 Hz, H-2), 4.65 (*d*, *J* = 12 Hz, H-3), 6.12 (*s*, OMe-5), 7.70 (*s*, OAc-7, OAc-4′), 7.98 (*s*, OAc-3), 8.08 (*s*, Me-6). MS (*m/e*): 442 (24%) M^+; 223 (27), 222 (94), 181 (73), 180 (100), 178 (26), 152 (8), 136 (61), 107 (38).

2,2′-*Dihydroxy*-4,4′,6,6′-*tetramethoxy*-3,3′-*dimethylbenzophenone* (**4a**), mp 180–183° (EtOH). (M Found: 362.1353; $C_{19}H_{22}O_7$. Requires: 362.1366.) ν_{max}^{KBr} cm^{-1}: 3350, 3310, 1616, 1590, 1500. λ_{max}^{EtOH} nm: 243 inf., 270 (ε 23 500, 9400); $\lambda_{max}^{EtOH+NaOH}$ nm: 246 inf., 280 (ε 20 250, 10 850); $\lambda_{max}^{EtOH+AlCl_3}$ nm: 237 inf., 270 (ε 31 150, 14 100). ^{1}H NMR ($CDCl_3$, 60 MHz): τ 2.10 (*s*, 2 OH-2), 3.90 (*s*, 2 H-5), 6.00 (*s*, 2 Me-4), 6.20 (*s*, 2 OMe-6), 7.98 (*s*, 2 Me-3). MS (*m/e*): 362 (10%) M^+, 196 (10), 195 (100), 194 (63), 168 (13), 167 (9). *Diacetate* (**4b**). ^{1}H NMR ($CDCl_3$, 60 MHz): τ 3.58 (*s*, H-5), 3.65 (*s*, H-5′), 6.20 (*s*, 4 OMe), 7.72, 7.82 (2*s*, 2 OAc), 8.16, 8.17 (2*s*, 2 Me).

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